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STUDIES IN THE HALOGENATION OF ALIPHATIC COMPOUNDS

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FOREWORD

This report was prepared by the University of Sheffield, United Kingdom under Grant No. AF-EOARDC-61-7. The grant was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena", Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials".

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This report has been reviewed and is approved.

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ABSTRACT

The relative rates of the gas phase chlorination of n-hexane at the primary and secondary positions were studied and a rate expression obtained. The chlorination and bromination of 1,1,1-trifluoropentane and 1-fluorobutane have been studied in the gas phase using a static system. The reactions were studied at several temperatures and approximate values of the Arrhenius parameters for attack at each site in the molecules have been obtained. The results confirm earlier work and show that the CF_3 group exerts a very powerful deactivating effect on halogenation at adjacent sites. The chlorination and bromination of n-valeryl fluoride chloride and methyl valerate have been studied in the gas phase using a static system. The acyl group deactivates halogenation at adjacent methylene groups, but to a lesser extent at the α -position than would be expected on purely polar grounds. The gas phase reaction of fluorine and carbon tetrachloride with nitrogen as a diluent has been studied in a flow system. The extent of reaction was followed by determining the halide formed when unchanged fluorine and any fluorine monochloride produced was converted into hydrogen fluoride and hydrogen chloride. Preliminary studies of the gas phase chlorination of n-butyl acetate and methyl n-butyl ether have been made using a static system.

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SECTION I

THE CHLORINATION OF n-HEXANE IN THE GAS AND LIQUID PHASES

In their pioneering studies Hass and co-workers reported that chlorination of aliphatic hydrocarbons was less selective in the liquid phase than in the gas phase (Reference 1). In 1957 Russell reported a far more pronounced solvent effect (Reference 2). He found that certain solvents, particularly aromatic compounds, greatly increased the selectivity of liquid phase chlorination and he was able to show that the result could best be explained by assuming that the chlorine atom formed a charge transfer complex with the aromatic nucleus. Subsequently Walling and Mayahi found that carbon disulphide was a more powerful complexing solvent than any aromatic compound and chlorinations in this solvent were very selective (Reference 3). However, none of these results help to explain Hass' original observations in which the solvent phase reaction is less selective than that in the gas phase. In the present work the chlorination of n-hexane has been carried out in the gas and liquid phases over a range of temperatures. It was hoped to put Hass' qualitative observations on a more quantitative basis, and to obtain sufficient data to facilitate interpretation.

EXPERIMENTAL

The gas phase apparatus was similar to that used in previous work (Reference 4). Essentially it consisted of two preheating coils made of 6 mm O.D. tubing (total volume of each coil was 25 cc) which entered a mixing vessel with their jets opposed. The mixing vessel (75 cc) led on to a reaction spiral made of the same tubing (100 cc). A stream of chlorine mixed with nitrogen was led into one preheating coil, while another stream of nitrogen was bubbled through n-hexane (maintained at a known temperature) and then led into the other preheating coil. The combined gas stream emerging from the reaction coil was passed successively through tubes packed with thiosulphate crystal (to remove excess chlorine) and "soda-asbestos" (to remove the hydrogen chloride) before finally passing through a trap maintained at -78° in which the reaction products were condensed.

The experiments in the liquid phase were carried out in a reaction vessel with a long narrow capillary through which gaseous hydrogen chloride formed during the reaction could escape. The reaction vessel was always filled completely so that at the start of the reaction there was no vapor in contact with the solution. Hexane was placed in the reaction vessel which was then immersed in a bath at the required reaction temperature. The chlorine was dissolved in carbon tetrachloride and this solution was immersed in the same constant temperature bath. As soon as both solutions had reached the required temperature the carbon tetrachloride was added rapidly to the hexane in the dark. When the reactants were properly mixed the reaction vessel was illuminated by a 100 watt tungsten lamp for 20 minutes.

The analysis of the reaction products from both series of reactions were achieved using the gas chromatography apparatus previously described. Approximately ten analytical runs were made for each experiment.

Chlorination of n-Hexane - Relative Selectivities

(Mean Values at Each Temperature)

GAS PHASE:

n-Hexane (10 parts) + Chlorine (1 part) + Nitrogen (350 parts)

RS	log RS	T°K	(T) ⁻¹
2.74	0.437	485	0.00206
2.79	0.4465	395	0.00254
3.03	0.481	349	0.00286
3.10	0.491	313	0.00320
4.87	0.688	275	0.00364

SOLVENT PHASE:

n-Hexane (10 parts) + Chlorine (1 part) + Carbon Tetrachloride (5 parts)

RS	log RS	T°K	(T) ⁻¹
2.2	0.342	312	0.00321
2.3	0.362	295	0.00339
2.27	0.356	273	0.00366
2.49	0.396	258	0.00388
2.87	0.457	240	0.00417
3.54	0.548	203	0.00493

DISCUSSION

All the individual analytical runs have been combined in a "least Squares" calculation to yield the following rate expressions:

$$\left(\frac{k_s}{k_p} \right)_{\text{gas}} = 2.0 \pm 0.1 \exp (304 \pm 50 \text{ cal}/RT)$$

$$\left(\frac{k_s}{k_p} \right)_{\text{liquid}} = 0.8 \pm 0.2 \exp (600 \pm 65 \text{ cal}/RT)$$

These results show that the greater selectivity of gas phase chlorination at normal temperatures is due to the ratios of the kinetic terms in the rate expressions. In fact there is a greater difference between the activation energies for attack at the primary and secondary positions in the liquid phase. The results completely confirm the qualitative picture given by Hass' original results, although the numerical values are slightly different. The results also show that Russell's recent assumption that the rate constants for the reactions of chlorine atoms in the gas and "non-complexing" solvent phase, are the same, must be treated with reserve (Reference 5).

There are two simple explanations that have been offered to explain this difference in gas and liquid phase chlorination. The first of these is a modification of the Frank-Rabinowitch cage hypothesis. The rate of chlorination in the gas phase is of the order of 10^{13} mole⁻¹ cm³ sec⁻¹ at room temperature which is comparable with the rate of diffusion of chlorine atoms in the liquid phase. Thus a chlorine atom caged by solvent molecules will be held at a particular site long enough for there to be a high probability of reaction even though there are more reactive sites elsewhere. The present results are not consistent with such an explanation. According to such a theory it would be expected that the selectivities in the gas and liquid phases would become more similar as the temperature rose, and this is clearly not the case.

The alternative explanation is that the chlorine atom is solvated (that is, forms a weak charge transfer complex even with solvents regarded as non-complexing by Russell). This explanation was originally dismissed because the liquid phase reaction is less selective than the gas phase reaction, but the present results show that this is due to a kinetic energy rather than potential energy change. For a reaction which is endothermic in the gas phase, the change to a solvent in which one of the reactants (for example, chlorine atoms), but not the activated complex, is solvated, would have the effect of increasing the overall activation energy, without increasing the selectivity. However Walling has suggested that if a reaction is exothermic in the gas phase, but becomes endothermic in the solvent phase as a result of solvation, then it is reasonable to expect a change in selectivity (Reference 3). A change in the difference in activation energy between two sites is particularly likely if the attack at both sites is exothermic in the gas phase but in the solvent phase one becomes endothermic. In the present case the activation energies for attack at the primary and secondary hydrogen atoms are approximately 700 and 300 cal moles⁻¹ in the gas phase. Thus if the heat of solvation of the chlorine atom is of the order of -0.5 kcal moles⁻¹ we would have just such a situation.

The present results rule out the "cage" hypothesis as the sole explanation of the difference in selectivities in the gas and liquid phase reactions; but it seems probable that the large relative difference in the kinetic energy terms are due to effects of this kind. The change in the relative activation energies can be accommodated by the "solvation" hypothesis if it is assumed that the heat of solvation of a chlorine atom in the hexane/carbon tetrachloride system is of the order of -0.5 kcal mole⁻¹.

SECTION II

THE HALOGENATION OF 1,1,1-TRIFLUOROPENTANE

In the 1940s Henne and his co-workers published a series of papers describing the chlorination of alkanes containing CF_3 - and $-\text{CF}_2$ -groups (References 6, 7, 8, 9). These results are of very considerable general interest. The trifluoromethyl-group provides an example of a substituent exerting a powerful inductive, but negligible resonance or mesomeric effects. For this reason it is a particularly valuable group to study when directive influences are being investigated. Henne found that chlorination was powerfully directed away from highly fluorinated groups and this result forms the starting point of most discussions on the importance of polar effects in chlorination. The present work was aimed at repeating Henne's work using the much more precise analytical equipment now available and extending the study to bromination. 1,1,1-Trifluoropentane was chosen, rather than the trifluorobutane previously studied by Henne. It was hoped that the carbon atom at the far end of the molecule would be unaffected by the substituent fluorine atoms and the compound could be regarded as n-butane substituted in the 1-position with a trifluoromethyl-group.

EXPERIMENTAL

A static system was employed similar to that previously used in the study of trichloromethyl radicals (Reference 10). Analysis of the products was achieved by gas chromatography using a Griffen and George D6 apparatus. The detector in this instrument is a gas density balance and this greatly facilitated the work, because it was no longer necessary to synthesize pure specimens of each of the halogenated products in order to calibrate the detector. Identification of the reaction products was achieved by halogenating a large liquid sample (circa 1g), and then separating the four halogenated products on a semi-preparative scale (0.5 g samples) gas chromatography apparatus. Carbon tetrachloride solutions of each peak were then examined with an A. E. I. Ltd., RS2 nuclear magnetic resonance spectrometer. Identification of the halogeno-1,1,1-trifluoropentane from their nuclear magnetic resonance spectra was a very easy matter.

APPARATUS AND EXPERIMENTAL TECHNIQUES

A conventional vacuum line was employed. The reaction vessel was of "Pyrex" and 286 cc capacity. The reactants were carefully "degassed" and the reaction vessel was filled with the halogen and the alkane at known pressures. The reaction vessel was surrounded with a heated bath (water or liquid paraffin) and then irradiated with light from two 150 watt lamps. At the end of the run, the reaction products were condensed into a small trap from which samples could be taken for injection into the gas chromatography apparatus.

REACTANTS

1,1,1-Trifluoropentane was prepared from n-valeric acid by treatment with sulphur tetrafluoride according to the directions of Hasek, Smith and Engelhardt (Reference 11). The compound had bp 39°C , $n_D^{28.5}$ 1.3101 and was shown by gas chromatography to contain a trace (2 percent) of some low boiling material as the only impurity. 1-Fluorobutane was prepared from 1-bromobutane by treatment with potassium fluoride in ethylene glycol (Reference 12), and had bp $32-33^\circ\text{C}$.

CHLORINATION OF 1,1,1-TRIFLUOROPENTANE

The reaction vessel was charged with the pentane (circa 6 parts) and chlorine (circa 1 part) at a total pressure of 250 mm. Experiments were carried out at four different temperatures and the proportions of the chlorinated products are tabulated as relative selectivities (RS_4^X).

Temp.	No. of runs	$CF_3CH_2\text{---}CH_2\text{---}CH_2\text{---}CH_3$			
0°	5	0.03±0.01	1.07±0.07	4.46±0.10	1
20	9	0.03±0.004	1.11±0.16	4.55±0.11	1
60	7	0.04±0.01	1.21±0.03	4.38±0.05	1
230	4	0.06±0.01	1.29±0.11	4.01±0.16	1

There were three principal peaks besides that of the starting material, on the gas chromatograms. About 2 cc of the trifluoropentane was chlorinated in the liquid phase and approximately 0.7 cc samples were injected into a large scale gas chromatography apparatus. From this apparatus it was possible to obtain on elution, specimens of the three larger product peaks. These were dissolved in carbon tetrachloride and their nuclear magnetic resonance spectra observed. The three samples were readily identified as 3-chloro, 4-chloro- and 5-chloro-1,1,1-trifluoropentane eluted in that order. Besides these main product peaks there was a very small peak on the analytical chromatograms between the starting material and the 3-chloro-isomer. This peak was far too small for its collection to be practical, but it was assumed to be 2-chloro-1,1,1-trifluoropentane.

BROMINATION OF 1,1,1-TRIFLUOROPENTANE

The reaction vessel was charged with the pentane (circa 20 parts) and bromine (circa 1 part) at a total pressure of circa 200 mm. The reaction products are listed as selectivities relative to carbon atom 3 (RS_3^X) because the relative rate of attack on carbon atom 4 was very small and hence the analysis of the rate of attack on this site by far the least accurate.

Temp.	No. of runs	$CF_3CH_2\text{---}CH_2\text{---}CH_2\text{---}CH_3$			
40°	15	-	0.118±0.008	1	0.005±0.002
76	13	-	0.132±0.007	1	0.005±0.002
155	5	-	0.148±0.007	1	0.011±0.002
200	5	-	0.160±0.004	1	0.015±0.001
230	7	-	0.204±0.020	1	0.019±0.001

There were three principal product peaks followed by two much smaller peaks on the analytical gas chromatograms in addition to the unchanged starting material. Using the large scale gas chromatograph it was possible to obtain specimens of the three principal product peaks and to examine their nuclear magnetic resonance spectra. By this means the second and third peaks were unambiguously identified as 3-bromo and 4-bromo-1,1,1-trifluoropentane. The very small fourth peak was assumed to be 5-bromo-1,1,1-trifluoropentane. The small first peak could not be identified from either its nuclear magnetic resonance nor its infrared spectra. Its elution time corresponded with that expected for 2-bromo-1,1,1-trifluoropentane but the spectra showed quite convincingly that it did not have this structure (in fact the nuclear magnetic resonance spectrum showed it was not a derivative of trifluoropentane; changing the carrier gas in the gas density balance chromatograph showed it had a smaller molecular weight than the bromotrifluoropentanes). The amount of this product varied from run to run at the same temperature, suggesting that it may have been due to some unrecognized impurity in the reactants. This unidentified peak may have masked traces of the expected 2-bromo-1,1,1-trifluoropentane, but if so the amount of bromotrifluoropentane was very small indeed. The remaining peak on the gas chromatograms was very small and extremely high boiling. It may have been a dibromotrifluoropentane but it was present in too small a quantity to enable it to be isolated and it was in too small a quantity to have any appreciable effect on the results.

BROMINATION OF 1-FLUOROBUTANE

The reaction vessel was charged with 1-fluorobutane (10 parts and bromine (1 part) at a total pressure of circa 150 mm. Experiments were carried out at four different temperatures and the results are tabulated below as relative selectivities (RS_4^X).

Temp.	No. of runs	FCH ₂ —————CH ₂ —————CH ₂ —————CH ₃			
62°	10	11.3±1.4	9.5±1.0	146±13	1
107	8	15.5±1.6	14.4±1.3	201±17	1
160	7	6.7±1.5	4.7±0.9	63±8	1
185	7	8.7±0.6	7.3±0.5	81±8	1

The identification of the bromofluorobutanes has been described previously. (Reference 13).

DISCUSSION

Following the practice of previous papers of this series the relative rates of halogenation at each site or relative selectivities are compared in Table 1.

TABLE 1
THE HALOGENATION OF 1-FLUOROBUTANE AND 1,1,1-TRIFLUOROPENE.
EXPRESSED AS RELATIVE SELECTIVITIES - RS_p^{x13}

Chlorination 75°				Bromination 150°		
X =	H	F	CF ₃	H	F	CF ₃
XCH ₂	1	0.9	0.04	1	9	<1
CH ₂	3.6	1.7	1.2	80	7	7
CH ₂	3.6	3.7	4.3	80	90	90
CH ₃	1	1	1	1	1	1

The chlorination results completely confirm the earlier qualitative work of Henne and his co-workers, and it is impossible not to admire this previous study which involved a difficult synthesis of starting material followed by separation of the reaction products by distillation and their identification by chemical methods. The present work utilized the comparatively easy one step synthesis of 1,1,1-trifluoropentane from valeric acid and sulphur tetrafluoride followed by the quantitative separation of the reaction products using gas chromatography and their identification by nuclear magnetic resonance spectroscopy.

Table 1 shows, as expected that a CF₃-group exerts a deactivating effect on chlorination and bromination at a β -carbon atom. This deactivation is of the same order as that exerted by a substituent fluorine atom. The inductive effect (-I) of a trifluoromethyl group and a fluorine atom are of the same order (cf the dissociation constants of fluoroacetic acid pK 3.3 and 3,3,3-trifluoropropionic acid pK 3.1). Halogenation is almost completely inhibited at the carbon atom α to the trifluoromethyl group, in marked contrast to halogenation at the carbon atom α to a fluorine atom. The relatively high reactivity of hydrogen atoms attached to the same carbon atom as a halogen has been attributed to the ability of the substituent halogen to conjugate with the incipient trivalent carbon atom and has been discussed at length in previous papers (Reference 13). The trifluoromethyl group exerts about the same inductive effect as a substituent fluorine atom but it is unable to stabilize the incipient radical by conjugation.

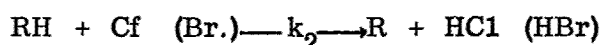
The relative selectivities listed in Table 1 are in very good accord with the predictions made in Part II of the present series (Reference 3) and with the subsequent more comprehensive discussion (Reference 4). Greater weight could be placed on these arguments if the changes in activation energy brought about by a substituent could be measured. The present work has been carried out over a fairly wide temperature range and it is possible to

calculate very approximate values for the Arrhenius parameters for chlorination and bromination at each site of these molecules (Table 2).

TABLE 2

APPROXIMATE VALUES FOR THE ARRHENIUS PARAMETERS FOR THE
CHLORINATION AND BROMINATION OF 1-FLUOROBUTANE AND
1,1,1- TRIFLUOROPENTANE

($\log A_2$ in $\text{mole}^{-1} \text{ cm.}^3 \text{ sec}^{-1}$; E_2 in kcal mole^{-1})



Chlorination								
α β γ δ								
$X-CH_2-CH_2-CH_2-CH_3$								
	$\log A_2$	E_2	$\log A_2$	E_2	$\log A_2$	E_2	$\log A_2$	E_2
X = H	<u>13.2</u>	<u>0.8</u>	<u>13.3</u>	<u>0.3</u>	<u>13.3</u>	<u>0.3</u>	13.2	0.8
X = F	13.1	0.8	13.2	0.6	<u>13.4</u>	<u>0.3</u>	13.2	0.8
X = CF ₃	12.2	2.0	13.0	0.6	<u>13.3</u>	<u>0.3</u>	12.8	0.5
Bromination								
X = H	<u>13.1</u>	<u>13.4</u>	<u>13.6</u>	<u>10.2</u>	<u>13.6</u>	<u>10.2</u>	<u>13.1</u>	<u>13.4</u>
X = F	13.2	11.6	13.1	11.5	<u>13.6</u>	<u>10.2</u>	13.0	13.0
X = CF ₃	-	?	13.2	11.0	<u>13.6</u>	<u>10.2</u>	13.1	13.0

On the basis of the relative selectivities it appeared that the substituent fluorine atom or the trifluoromethyl group have no effect on the rate of halogenation at the terminal δ carbon atom and very little influence at the γ position. In order to calculate absolute values of the reaction rates at each site it was necessary to assume that the rate of halogenation at either the γ or the δ position was the same as that for the primary or secondary positions in n-butane. By taking the values for the chlorination from the data of Knox and Nelson (Reference 15) and for the bromination from the data of Fettis, Knox and Trotman-Dickenson (Reference 16) it was possible to calculate very approximate values for the other sites in 1-fluorobutane and 1,1,1-trifluoropentane (in the table underlined numbers represent the assumed values). The values in Table 2 are very approximate because of the large scatter in the experimental results and because the differences in the relative rates over the temperature ranges studied are comparatively small. Nonetheless the table forms a very consistent overall picture and provides strong confirmatory evidence for the theoretical ideas developed previously. The bromination data for the γ and δ -positions in butyl fluoride and 1,1,1-trifluoropentane represent the first time the relative rates of attack at primary and secondary hydrogen atoms in the same molecule have been obtained over a temperature range (the underlined numbers in Table 2 come from ethane and the secondary position in n-butane). It is very satisfactory to find that the present results are so close to the previous interpolated figures.

SECTION III

THE HALOGENATION OF DERIVATIVES OF n-VALERIC ACID

Early work on the halogenation of carboxylic acids and their derivatives was complicated by simultaneous ionic and radical reactions. The Hell-Volhard-Zelinsky reaction represents the isolation of the ionic path and yields exclusively the α -halogeno derivative. Micharl and Garner appear to have been the first to report that chlorination promoted by light yields all possible isomers with the α -isomer in the smallest amount (Reference 17). Much later Kharasch and Brown pointed out there are homolytic and heterolytic reactions which yielded different products (Reference 18). Since then the atomic chlorination of aliphatic acyl chlorides has been studied by Bruylants and his co-workers (Reference 19) Den Hertog and his co-workers (Reference 20) and by Brown and Ash (Reference 21). This work produced further controversy. The chlorinations were carried out in the gas phase, in the liquid phase and in the liquid phase using sulphuryl chloride. The great difficulty encountered by all three groups of workers was the accurate separation and estimation of the products. Faulty separation led Bruylants to believe that the rate of chlorination at the β -position was abnormally high, and in order to account for this he proposed a cyclic transition state. However neither Brown and Ash, nor Den Hertog, De vries and Van Bragt observed particularly rapid attack at the β -position of propionic or butyric acids and in subsequent work by Bruylants to some extent retracts his original ideas (Reference 22). By far the most satisfactory study is reported in a second paper by Den Hertog (Reference 23). He solved the problem of isolating a number of high boiling, thermo-labile products by converting the acid chlorides into esters and separating the esters by counter current distribution. According to these results the chloro-acyl group deactivates not only the α -position but to a lesser extent the β -position and even the γ -position very slightly.

In view of the contradictory nature of this previous work, reinvestigation using the more refined techniques of analysis and identification now available is clearly desirable. Even the one point on which the previous workers agree, that is, the very low reactivity of the α -position, is, as Walling points out (Reference 24), not really in accord with expectation and could do with fresh appraisal. The present work is intended to be very much more quantitative than the previous studies and n-valeryl derivatives were chosen because they could be regarded as n-butane substituted in the 1-position and be compared with previous studies in this series. n-Valeryl fluoride and methyl valerate were chlorinated in addition to valeryl chloride so that some measure of the relative directing influence of the carbonyl group could be assessed. Finally bromination was also studied because previous work has shown how much more information can be obtained if both forms of halogenation are studied simultaneously. There is very little previous data on atomic bromination.

EXPERIMENTAL

The chlorinations and bromination were carried out in a conventional vacuum line. The reaction vessel was made of "pyrex". The reactants were carefully "degassed" and the reaction vessel was filled with the halogen and the valeryl derivative at known pressures. The reaction vessel was surrounded with a heated bath (water or liquid paraffin) and then irradiated with light from two 150 watt lamps. At the end of the run the reaction products were condensed into a small trap from which samples could be taken for injection into the chromatography apparatus. Analysis was carried out on a Griffen and George D6 apparatus employing a density balance as detector. Identification of the products was achieved by two methods. The first required the unambiguous synthesis of the halogeno-compound; a very small trace of this compound added to the reaction products and on running a new chromatograph it was possible to see which peak had been enlarged. The second method of identification required the halogenation of a large liquid sample (circa 1g) which was then

chromatographed on a semi-preparative scale (0.5 cc samples) apparatus. The peaks were collected as they were eluted and carbon tetrachloride solutions of each peak were then examined with an A.E.I. Ltd., RS2 nuclear magnetic resonance spectrometer.

Reactants - n-Valeryl chloride was prepared from commercial valeric acid by treatment with thionyl chloride, and had $b p^\circ$, $n_D^{22^\circ}$, n-valeryl fluoride was prepared from the chloride by treatment with anhydrous potassium fluoride and had $b p^\circ$, $n_D^{22^\circ}$.

CHLORINATION OF n-VALERYL CHLORIDE

A mixture of n-valeryl chloride (10 parts) and chlorine (1 part) at a total pressure of approximately 250 mm were illuminated for two hours by two 150 watt tungsten lamps. The reaction vessel was surrounded by a bath of purified liquid paraffin heated to the required temperature. The results are expressed as relative selectivities:

Temp.	No of runs	$\text{ClOC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$			
55-60°	10	0.16±0.01	2.08±0.11	3.96±0.10	1
130	10	0.18±0.01	1.99±0.10	4.06±0.10	1

At the end of the reaction the entire contents of the reaction vessel were condensed into a trap containing a slight excess of anhydrous methanol. The trap was allowed to warm up to room temperature and the resultant mixture of methyl valerate and chloromethyl chloro-valerates were analyzed on a silicone column. Besides unchanged methanol and methyl valerate there were four chloro-ester peaks on the chromatogram. The reasonable supposition was that these would be eluted in order of their boiling points, that is, 2-chloro-, 3-chloro-, 4-chloro- and 5-chloro- respectively. This supposition was confirmed by the individual addition of the 2-, 3-, and 5-chloro-esters.

CHLORINATION OF n-VALERYL FLUORIDE

A mixture of n-valeryl fluoride (10 parts) and chlorine (1 part) at a total pressure of approximately 250 mm was illuminated for two hours by two 150 watt tungsten lamps. The results are expressed as relative selectivities:

Temp.	No. of runs	$\text{FOC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$			
65-70°	8	0.08±0.01	1.57±0.08	4.20±0.12	1
100-102	8	0.10±0.01	1.46±0.04	3.85±0.12	1
130	10	0.12±0.01	1.70±0.05	4.22±0.08	1
160	8	0.08±0.01	1.24±0.03	3.53±0.13	1

The products were isolated exactly as for n-valeryl chloride; thus the compounds being analyzed were identical to those in the previous experiment and no additional identification was necessary.

CHLORINATION OF METHYL n-VALERATE

A mixture of methyl n-valerate (10 parts) and chlorine (1 part) at a total pressure of approximately 250 mm was illuminated for two hours by two 150 watt tungsten lamps. The results are expressed as relative selectivities:

Temp.	No. of runs	$\text{CH}_3\text{—O—C: O—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$			
55-60°	7	0.07±0.01	0.43±0.01	2.42±0.11	3.56±0.14
100-104	8	0.09±0.01	0.42±0.02	2.36±0.09	3.37±0.08

The analysis was carried out as before only no methanol was added. Thus the four methyl chlorovalerate peaks on the chromatograms were the same as before. When the same silicone column was used only four product peaks were obtained, but the peak which corresponded to the 3-chloroester was larger than expected (RS_5^3 - 3.07 instead of around 2.5 as expected). By changing the solvent on the column to tricresyl phosphate an additional peak was resolved between the 2-, and 3-chloroesters. This was shown to be chloromethyl valerate by the addition of authentic material to the reaction mixture.

BROMINATION OF METHYL n-VALERATE

A mixture of methyl n-valerate (5 parts) and bromine (1 part) at a total pressure of approximately 250 mm was illuminated by a 300 watt and a 150 watt lamp for three hours. The results are expressed as selectivities relative to carbon atom 4.

Temp.	No. of runs	$\text{CH}_3\text{OOC—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$			
50°	2	0.77±0.03	0.43±0.01	1	?
160°	11	0.53±0.03	0.45±0.02	1	0.013±0.004

The analysis was carried using a column packed with tritoluyl phosphate on "Celite". The product mixture from the run at 50° contained too little of the *s*-isomer for accurate estimation. The peaks were identified by the addition of authentic specimens of the α and δ isomers. The remaining peaks were assumed to be the β and γ isomers eluted in that order. Only traces of bromomethyl valerate was detected.

BROMINATION OF n-VALERYL CHLORIDE

A mixture of n-valeryl chloride (5 parts) and bromine (1 part) at a total pressure of 250 mm were irradiated by a 300 watt and a 150 watt tungsten lamp for three hours. The results are expressed as relative selectivities:

Temp.	No. of runs	$\text{ClOC—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$			
160°	6	0.38±0.11	0.42±0.01	1.0	0.013±0.001

The analyses were performed using a column packed with tritoluyl phosphate (20 percent) on "Celite". The products of the reaction were condensed into a slight excess of anhydrous methanol (cf chlorination experiment) and the analysis was made of the resulting bromo esters. Their identification is discussed above.

BROMINATION OF n-VALERYL FLUORIDE

A mixture of n-valeryl fluoride (10 parts) and bromine (1 part) was irradiated by two 150 watt lamps for three hours. The results are expressed as relative selectivities.

Temp.	No. of runs	FOC-CH ₂ —CH ₂ —CH ₂ —CH ₃			
150°	6	0.42±0.04	0.33±0.01	1.0	-

The analysis was carried out on a column packed with silicone on "Celite"; bromo-acyl fluorides being analyzed directly. The order of elution was assumed to be the same as that established in all the other experiments.

DISCUSSION

Comparison of the present chlorination results with the previous work gives a superficial appearance of similarity. The acyl group strongly deactivates the α -position and has some deactivating influence at the β -position. However in contrast to the liquid phase results of Smit and Den Hertog there is no evidence of deactivation at the γ -position. On the other hand the present results confirm the latter workers conclusions that there is no activation at the β -position. In Table 3 the present chlorination results are compared with our previous data on the chlorination of the n-butyl halides and of 1,1,1-trifluoropentane. It will be seen that the combined data forms a very consistent picture. It is clear that in the gas phase none

TABLE 3

RELATIVE SELECTIVITIES RS_p^x FOR THE CHLORINATION OF
THE n-BUTYL HALIDES, 1,1,1-TRIFLUOROPENTANE AND
DERIVATIVES OF n-VALERIC ACID AT 75°

X—CH ₂ —CH ₂ —CH ₂ —CH ₃					
x = H		1	3.6	3.6	1
F		0.9	1.7	3.7	1
Cl		0.8	2.1	3.7	1
Br		0.4	-	3.6	1
CF ₃		0.04	1.2	4.3	1
COF		0.08	1.6	4.2	1
COC1		0.2	2.1	3.9	1
COOCH		0.4	2.4	3.6	1

of the substituents have an appreciable effect at the γ -position. Deactivation at the β -position by the carbonyl group is of the same order as that induced by a halogen atom. At the α -position

the carbonyl group is more deactivating than a halogen atom, but less deactivating than the trifluoromethyl group. Since a methoxy carbonyl group exerts a more powerful electron withdrawal than the trifluoromethyl group, this means that the incipient radical must be stabilized to some extent by resonance (see Figure 1). Evidence for this effect has previously been obtained from other radical reactions, but when chlorination was studied in isolation this phenomenon was masked by the powerful inductive effect.

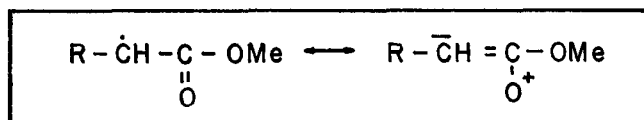


Figure 1. Resonance Stabilization

Comparison of the relative selectivities for the chlorination of valeryl fluoride, chloride and methyl valerate throws an interesting light on the way in which the remote group modifies the predominate influence of the carbonyl. The results show that there is no tendency for the halogen atoms adjacent to the carbonyl group to reduce its electron pull by means of their (+M) mesomeric effect. Instead their inductive effect (-I) supplements the inductive pull of the carbonyl.

Table 4 compares the present bromination results with our previous data on the bromination of the n-butyl halides and of 1,1,1-trifluoropentane. The value of doing both chlorination and bromination studies is again very clearly demonstrated. The importance of the resonance stabilization depicted in Figure 1 is now clearly manifested. The decreasing importance of polarity and increasing importance of relative bond strength in determining the selectivity

TABLE 4
RELATIVE SELECTIVITIES RS_p^{X} FOR THE BROMINATION OF
THE n-BUTYL HALIDES, 1,1,1-TRIFLUOROPENTANE AND
DERIVATIVES OF n-VALERIC ACID AT 160°

X ————— CH ₂ ————— CH ₂ ————— CH ₂ ————— CH ₃				
X = H	1	80	80	1
= F	9	7	90	1
= Cl	34	32	(80)	1
= CF ₃	1	7	90	1
X = COF	34	26	(80)	1
= COCl	30	33	(80)	1
= COOCH ₃	42	36	(80)	1

of bromination, in comparison with chlorination, has been discussed in detail previously (Reference 13,14). In all respects the bromination results are in excellent accord with the chlorination results and the combined results provide a striking example of the correctness of existing theory (Reference 14).

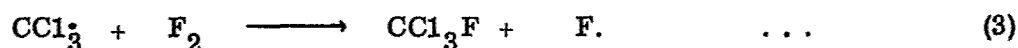
SECTION IV

THE REACTION OF FLUORINE ATOMS WITH CARBON TETRACHLORIDE

Previous work in this laboratory has been devoted to the study of the abstraction of hydrogen from aliphatic hydrocarbons by halogen atoms or trichloromethyl radicals. A fairly complete picture of this process has been developed. The present investigation is the first of a series in which the abstraction of halogen atoms from aliphatic compounds will be studied.

The fluorination of carbon tetrachloride has been studied qualitatively by Ruff (Reference 25) and by Simons (Reference 26). Ruff found little reaction at room temperature and when the carbon tetrachloride was refluxed, explosions occurred. Both Ruff and subsequently Simons carried out the heterogenous fluorination of carbon tetrachloride, bubbling the gaseous fluorine through refluxing carbon tetrachloride and adding various "catalysts" such as iodine, arsenic or bromine. Simons also studied the fluorination of difluorodichloromethane in the gas phase, again in the presence of "catalysts". The notable feature of this work was that difluorodichloromethane was much less reactive than carbon tetrachloride. The present work was planned in the light of these qualitative reports. However in the event they proved rather misleading.

If fluorine and carbon tetrachloride vapor react together the following steps represent the expected reaction paths:



The possible chain terminating steps are as follows:



The reaction chain contains no branches, so provided there is no thermal branching, the concentration of radicals cannot exceed the concentration of fluorine atoms in equilibrium at the reaction temperature. As this is very small we can neglect Reaction 5. Reaction 3 is exothermic to the order of 60 kcals/mole and will therefore have no appreciable activation energy. At room temperature the concentration of molecular fluorine, and the concentration of trichloromethyl radicals must certainly be much less than this. Therefore provided the concentration of fluorine is at least as great as the concentration of carbon tetrachloride the rate of Reaction 4 must be vanishingly small, since all the trichloromethyl radicals will react by Reaction 3 before they have a chance of meeting a fluorine atom. (In practice a tenfold excess of fluorine has been employed in the present work). This leaves Reaction -1, that is, the recombination of fluorine atoms as the only chain terminating step. If this argument is correct we would expect very long chains and this is in accord with the

experimental results. We thus have an exceptionally simple system and making the usual steady assumptions we obtain the following expression for the rate of Reaction 2.

$$\frac{d[\text{FCI}]}{dt} = k_2 \frac{k_1}{k-1} F_2^{\frac{1}{2}} [\text{CCl}_4]$$

The ratio $k_1/k-1$ is the dissociation constant of fluorine, and since the reaction chain neither increases or decreases the number of fluorine atoms we are quite justified in using the value obtained from equilibrium studies.

EXPERIMENTAL

Fluorine was used directly from a generator, but the 10 amp cell was run at about 1 amp for twenty-four hours and then at maximum current for a further three hours before each reaction run. The exclusion of oxygen from the fluorine was vital and in view of the consistency of the results we believe that oxygen had been eliminated. In the initial experiments when the cell was only run at three amps for an hour the reaction was very much slower and the results were erratic. The fluorine passed through a trap at -70° to remove hydrogen fluoride and was then joined by a stream of "oxygen free" nitrogen. The carbon tetrachloride was vaporized by bubbling a stream of nitrogen through the liquid which was maintained at a constant temperature. The reaction vessel consisted simply of a T-piece in which the carbon tetrachloride and fluorine streams met at right angles. The T-piece and the tubes leading into it were immersed in a thermostat. The combined flow passed along 3 cms of 3/16" O.D. copper tubing still in the thermostat before being led directly into a trap at -70° . Unchanged carbon tetrachloride and trichlorofluoromethane condensed in the trap while the fluorine monochloride and unreacted fluorine passed on to a heated column into which excess hydrogen was also led. The reaction occurred as an actual flame and the hydrogen fluoride and hydrogen chloride were collected in a series of traps cooled by liquid nitrogen. When the run was completed, heated hydrogen was passed through the traps and then through 2N sodium hydroxide solution free from carbonate (it was not possible to pass the reaction gaseous directly through alkali because the height of liquid required to ensure complete absorption of the hydrogen halides caused too much back pressure). The fluoride was determined by acidification of a measured portion of the solution followed by the addition of excess of a standard calcium solution and back titration with standard EDTA. The calcium fluoride was given twenty-four hours to separate and care was taken to exclude carbon dioxide. The chloride was determined spectrophotometrically by a modification of the method of Kitano and Tsubota (Reference 27).

Five runs at 20°C are tabulated. Each run was of 20 minutes (± 10 secs) duration and the volume (V) of the reactor was 5 cc. Since the reaction only went to 10 percent or less a plot of carbon tetrachloride concentration against $([\text{FCI}] U^{3/2} [\text{F}_2]^{-1/2} 10^{-2})$ gave a straight with a slope equal to $1/K^{1/2} k_2 V \times 60$.

Concentrations in moles/min.			Flow Rate (u) $\text{FCI} \times U^{3/2}$	
$\text{F}_2 \times 10^5$	$\text{CCl}_4 \times 10^5$	$\text{FCI} \times 10^7$	cc/min.	$\text{F}_2 \times 10^2$
13.27	0.98	8.82	213	2.38
16.96	1.2	11.59	214	2.79
18.46	2.25	19.80	225	4.81
15.11	3.28	26.50	221	7.10
11.80	3.5	27.40	227	8.63

DISCUSSION

The fact that the experimental results lay on a straight line gave strong support to the rate equation discussed above. Calculating K from the data of Cole, Farber and Elverum (Reference 28) gave $k_2^{293} = 4 \times 10^{13} \text{ moles}^{-1} \text{ cc sec}^{-1}$. This is a very reasonable result and if the pre-exponential factor is of the order of 10^{15} this gives an activation energy of 2-1/2 - 3 kcals/mole which is also of the expected order.

In conclusion it can be said that this use of the thermodynamic dissociation constant to determine atom concentrations in a chain reaction is only possible because of the unique properties of fluorine. The comparatively low value for the bond dissociation energy of fluorine results in an appreciable concentration of fluorine atoms even at room temperature and fluorine atoms are uniquely reactive. As far as we are aware this work is the first successful attempt to determine the absolute rate of a reaction involving fluorine atoms and we hope to extend these studies to other fluorination reactions.

SECTION V

THE CHLORINATION OF DERIVATIVES OF n-BUTANOL

The chlorination of derivatives of n-butanol considered to be of interest as further examples of compounds of the type $X - CH_2 - CH_2 - CH_2 - CH_3$ where $X = CH_3O, CH_3COO$. The methoxy group would be expected to be deactivating on the β -position in virtue of its -I inductive effect, but at the α -position the resonance +M mesomeric effect would be in opposition to the inductive effect and it is much more difficult to predict the reactivity of this position. Such data as is available in the literature suggests that activation at the α -position is likely. The acetoxy group would be expected to be predominately electron withdrawing and hence deactivating.

EXPERIMENTAL

The Chlorination of n-Butyl Methyl Ether

In preliminary experiments n-butyl ether was chlorinated in the flow apparatus described in the chlorination of n-hexane. However two difficulties were encountered. The first was the thermal instability of α -chloro-ethers and the second was loss of product due to preferential condensation of the higher boiling isomers. The ether was therefore chlorinated in the same static system used in the study of the halogenation of 1,1,1-trifluoropentane. The ether (circa 5 parts) was reacted with chlorine (circa 1 part) and a pressure of about 180 m m. The reactants were heated to the required reaction temperature and then illuminated by 2 x 100 watt tungsten lamps. The products were collected and analyzed as before. There were five peaks on the chromatogram and these were assumed to be the expected five chloroethers. In fact assuming their order of elution corresponded to that of their expected boiling points the following results were obtained:

Temp. °C	No. of runs	$CH_3-O-CH_2-CH_2-CH_2-CH_3$				
70	15	6.0	6.3	1.4	3.8	1

These results seemed extremely reasonable. However attempts to confirm the identification by separation of the individual peaks has so far proved unsuccessful.

Chlorination of n-Butyl Acetate

n-Butyl acetate (10 parts) and chlorine (1 part) were irradiated with light from two 150 watt tungsten lamps. The results are expressed as relative selectivities.

Temp. °C	No. of runs	$CH_3CO-O-CH_2-CH_2-CH_2-CH_3$				
70	trial runs	trace	0.2	2.4	4.0	1

When analysis was attempted using a silicone packed column only three product peaks were detected. However a column packed with tritoluyl phosphate (20 percent) on "Celite" proved effective and all five expected chloro-derivatives were detected. Identification was achieved by the individual addition of 1-chloro- and 4-chlorobutyl acetate and n-butyl chloroacetate.

DISCUSSION

A considerable amount of data on the chlorination of n-butyl ether has been obtained. Chlorinations have been made at three different temperatures and competitive chlorinations with n-butane have been attempted. However the fact that none of the products can be identified by their N.M.R. spectra has held up further work. Until the mass spectra of each of the products has been obtained further work has been abandoned. The preliminary data on the chlorination of n-butyl acetate are very satisfactory and fit in well with existing theory. In due time it should be possible to complete a thorough study of this reaction and also of the bromination of n-butyl acetate.

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13. ABSTRACT The relative rates of the gas phase chlorination of n-hexane at the primary and secondary positions were studied and a rate expression obtained. The chlorination and bromination of 1,1, 1-trifluoropentane and 1-fluorobutane have been studied in the gas phase using a static system. The reactions were studied at several temperatures and approximate values of the Arrhenius parameters for attack at each site in the molecules have been obtained. The results confirm earlier work and show that the CF ₃ group exerts a very powerful deactivating effect on halogenation at adjacent sites. The chlorination and bromination of n-valeryl fluoride chloride and methyl valerate have been studied in the gas phase using a static system. The acyl group deactivates halogenation at adjacent methylene groups, but to a lesser extent at the α -position than would be expected on purely polar grounds. The gas phase reaction of fluorine and carbon tetrachloride with nitrogen as a diluent has been studied in a flow system. The extent of reaction was followed by determining the halide formed when unchanged fluorine and any fluorine monochloride produced was converted into hydrogen fluoride and hydrogen chloride. Preliminary studies of the gas phase chlorination of n-butyl acetate and methyl n-butyl ether have been made using a static system.			

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